SIMULATION FOR THE GAS CHROMATOGRAPHY OF METAL CHELATES WITH CARRIER CONTAINING LIGAND VAPOUR

BY

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ABSTRACT

In the gas chromatography of metal chelates, it has been found experimentally that the chromatograms of the chelate are improved by using the ligand vapour as a carrier-gas additive. The chromatographic process combined with a chemical reaction was simplified by the model which consists with the dissociation equilibrium and the partition equilibrium. The simulation was done with a digital computer. As a result, it is fuond that the properties of the simulated chromatogram corresponds to the experimental results.

1. Introduction

The studies on the gas chromatography of metal chelates using carrier gas containing ligand vapour have been previously reported[1-4]. In these studies, it was found that the ligand vapour suppresses the anomalous elution of the chelates, acting on the decomposed metal chelates in the stationary phase and gives an improved chromatogram. But, it has not been cleared how the mechanism of the chromatography is operated, by the method using ligand vapour as the carrier-gas additive.

This new method ("ligand-carrier method") is considered to be a kind of the reaction chromatography, which is defined for the reaction occurring in a chromatographic column. The various reaction chromatography have been investigated with the theoretical treatments[5-9]. In 1960, J. Kallen and E. Heilbronner[10] reported the theoretical treatment of the pattern of an elution chromatogram for a compound undergoing a decomposition in a column. Their reaction model was based on the irreversible decomposition in the column. However, the reaction mechanism in the ligand-carrier method should be considered a reversible equilibrium, because a back reaction is produced by the addition of the ligand vapour.

In this work, the chromatographic process of the ligand-carrier method has been investigated with a simplified model, which was constructed with a reversible equilibrium and an intermittent "plate" theory[11]. On the simulation of the elution chromatogram, a digital computer was used because of the characteristics of the problem. And then, the simulated chromatograms were obtained for the gas chromatography of metal chelate with carrier containing ligand vapour and with carrier not containing, respectively.

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2. MODEL: Process of the Reaction Chromatography

2-1. Chromatographic Process

An exact treatment of gas-liquid chromatography leads to excessively complicated mathematics. In the present paper, the chromatographic process was extremely simplified in order to recognize the pattern of the elution chromatogram. The model of the simplified process was based on the "plate" theory[11].
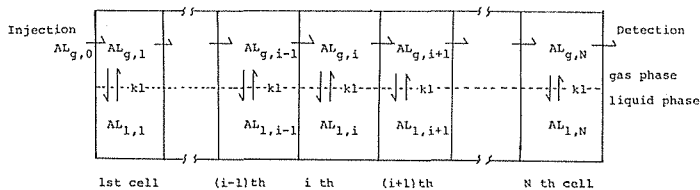

Fig. 1. Schematic diagram of the chromatographic process.

Fig. 1 shows a schematic diagram of the model for the chromatographic process. The column is considered as a device in which a number of elementary separation processes are linked. The total number of plates is N and the cell number is denoted by "i" ($i=1$, 2, 3,........., N). The cell of each plate consists of a moving gas phase and a stationary liquid phase. The injected solute is transferred with intermittent flow from $i=1$ to $i=N$ through the gas phase. In the transference, the solute is distributed between the gas and the liquid phases. The elution chromatogram is then obtainable from the relation between the amount of the solute and the number of transfer stages, t. In the simulation mentioned below, it is convenient to make t the number of transfer stages which means the sending t unit volumes of the carrier gas into the column.

2-2. Dissociation and Partition in a Cell

In the gas chromatography of metal chelate, the anomalous elution has ocasionally been observed at the front of the chelate peak. The appearance of the anomalous peak is attributed to the volatile ligand which is formed by the dissociation of the chelate in the stationary phase. From the facts, it is considered that the mechanism of the reaction chromatography is constructed with the dissociation equilibrium and the partition equilibrium of the metal chelate.

2-2-1. Dissociation Equilibrium in the Liquid Phase:

Relative amounts of metal chelate, AL_l, and relative amount of the proton of the stationary liquid, H_l^+, are equilibrated to relative amounts of the other species of the chelate and the ligand, A_l^+ and HL_l, in the stationary phase. The chemical equation is shown as follows,

$$\mathrm{AL}_l + \mathrm{H}_l^+ \overset{K3}{\rightleftarrows} \mathrm{A}_l^+ + \mathrm{HL}_l \tag{1}$$

where $K3$ is the equilibrium constant and the suffix, l, shows the species in the liquid phase. Here, $K3$ is defined as the apparent stability constant (see appendix II) of AL_l by the equation,

$$K3 = AL_l/(A_l^+ \cdot HL_l) \tag{2}$$

2-2-2. Partition Equilibria of AL and HL between the Gas Phase and the Liquid Phase:

The metal chelate and the ligand are volatile. Relative amounts of those solutes in gas phase are denoted by AL_g and HL_g, respectively, with the suffix, g. The apparent partition coefficients of $K1$ and $K2$ are defined by the equations (see appendix II),

$$K1 = AL_l/AL_g \tag{3}$$

and

$$K2 = HL_l/HL_g \tag{4}$$

In order to simplify the equations described below, $TO1$ is defined as the sum of AL_l and AL_g, and similarly $TO2$ is defined as the sum of HL_l and HL_g. Furthermore, $AK1$ and $AK2$ are defined for the apparent partition coefficients ($K1$ and $K2$), as shown in the following eq. (5) and (6). By using $TO1$ and $TO2$, the relation of eq. (3) and (4) are defined again by the following equations,

$$AL_l = TO1(K1/(K1+1)) = TO1/AK1 \tag{5}$$

$$HL_l = TO2(K2/(K2+1)) = TO2/AK2 \tag{6}$$

2-2-3. Increment of the Solute in a Cell under the Reaction:

In a chromatographic cell, the reaction procees by the mixed process which is constructed with the chemical equilibrium and the partition equilibrium. Here it is not necessary to consider, the partition equilibrium of the species, A^+ in the liquid, because A^+ is non-volatile.

Supposing the reaction to be fast, it is able to obtain the difference, D, between AL_l before the reaction and AL_l after the reaction. By combining eq. (2) with eq. (5) and (6), the next equation is obtained for the over all reaction in a cell.

$$K3 = \frac{(TO1-D)\dfrac{1}{AK1}}{(A_l^+ + D)(TO2+D)\dfrac{1}{AK2}} \tag{7}$$

From this equation, D is obtained as follows

$$D = \frac{-B + \sqrt{B^2 - 4 \cdot AK3 \cdot C}}{2 \cdot AK3} \tag{8}$$

where

$$AK3 = K3 \cdot AK1/AK2 \tag{9}$$

$$B = 1 + AK3(TO2 + A_l^+) \tag{10}$$

$$C = TO2 \cdot A_l^+ - TO1 \tag{11}$$

After the reaction which is represented by eq. (7), $TO1$ is changed to $(TO1-D)$, $TO2$ to $(TO2+D)$, and A_l^+ to $(A_l^+ + D)$, respectively. Therefore, AL_l, AL_g, HL_l and HL_g are finally obtained from eq. (5) and (6), as follows.

$$AL_l = (TO1-D)/AK1 \tag{12}$$

$$AL_g = (TO1-D) - AL_l \tag{13}$$

$$HL_l = (TO2 + D)/AK2 \tag{14}$$

$$HL_g = (TO2 + D) - HL_l \tag{15}$$

3. SIMULATION: Combining of the Chromatographic Process with the Reaction Process

The simulation for the present reaction chromatography is constructed under the basis of the combined model of the reaction process and the chromatographic process. The solutes in the gas phase are transfered according to the chromatographic process (section 2–1.). The equilibria of the solutes in each cell are realized according to the reaction (section 2–2.). The amounts of the solutes (eq. (12)–(15)) at $t=T$, are calculated with eq. (8) on the base of the data which are obtained at the preceding stage ($t=T-1$).

It is necessary to set various boundary conditions for the calculation representing the conventional method using helium carrier and the present method using ligand-vapour carrier.

3-1. The Conventional Method Using Helium as Carrier

In the conventional gas chromatography of metal chelates, helium is used as a carrier gas. Helium is treated only as the moving force of the gas phase, in this simulation.

In the case using helium as the carrier, the following equations are necessary for the calculation of $t=1$, as the initial condition (the amounts of the sample in the "i" th cell) and as the initial boundary conditions (the amounts of each species in the (N-1) cells).

$$AL_{g,i} = \begin{cases} 1 & i=1 \tag{16} \\ \\ 0 & i=2, 3, \ldots, N \tag{17} \end{cases}$$

$$AL_{l,i} = 0 \tag{18}$$

$$HL_{g,i} = 0 \tag{19}$$

$$\left. \begin{array}{l} \\ \\ \end{array} \right\} \quad i=1, 2, 3, \ldots, N$$

$$HL_{l,i} = 0 \tag{20}$$

$$A_{l,i}{}^+ = 0 \tag{21}$$

$AL_{g,i}$ at $i=1$ and $t=1$ is the amount of injected sample and is normalized to 1.0.

For the calculation of $t \geqq 2$, $AL_{g,i}$ and $HL_{g,i}$ at $i=1$ are necessary as the boundary conditions, except for $AL_{g,i}$ and $HL_{g,i}$ ($i \geqq 2$). These conditions are as follows,

$$Al_{g,i} = 0 \qquad i=1 \quad (t \geqq 2) \tag{22}$$

$$HL_{g,i} = 0 \qquad i=1 \quad (t \geqq 2) \tag{23}$$

$AL_{g,i}$ and $HL_{g,i}$ ($i \geqq 2$) at $t=T$ are set with the $AL_{g,i}$ and $HL_{g,i}$ ($i=1, 2, 3\ldots, N$-1) which are obtained at $t=T$-1.

In the calculation of each transfer stage, $AL_{g,i}$ and $HL_{g,i}$ at $i=N$ are obtained as the amounts of the eluted AL and the eluted HL, respectively. Finally, the plotted curves of $AL_{g,N}$ and $HL_{g,N}$ vs t are the simulated chromatograms of AL and HL which represent the chromatogram obtained in the conventional gas chromatography.

3-2. In the Case Using Ligand Vapour as Carrier-Gas Additive

In the gas chromatography of metal chelates with the ligand-carrier method, the

majority of the carrier gas is helium, and the carrier-gas additive is the same as the ligand of the metal chelate.   In the experiments, the additive is continuously supplied at the front of the column and the amounts of the supplied vapour is detected at the base line.

The conditions for HL are set for the case of the ligand-carrier method.   The other conditions are the same as the conditions represented by eq. (16), (17), (18), (21) and (22) in section 3–1., for all the cases of i and t.   Namely, the initial boundary conditions ($t=1$) are

$$HL_{g,i}=CLG$$ (24)

$$\left.\begin{array}{c}\\ \\\end{array}\right\} \quad i=1, 2, 3, \ldots\ldots, N$$

$$HL_{l,i}=CLL$$ (25)

and the boundary conditions ($t \geqq 2$) are

$$HL_{g,t}=CLG \qquad\qquad i=1$$ (26)

where CLG and CLL are the amount of the ligand vapour in the gas phase and in the liquid phase, respectively.   The relation between CLG and CLL is defined by the apparent partition coefficient of HL, $K2$ (see eq. (4)), as follows,

$$CLL=CLG \cdot K2$$ (27)

$AL_{g,N}$ and $HL_{g,N}$ are calculated from the assumption mentioned above.   In the case of $CLG \neq 0$, $HL_{g,N}$ is obtained for the amounts of the decomposed ligand by subtracting CLG from the total $HL_{g,N}$ which is actually used in the calculation because the total $HL_{g,N}$ is defined as the total sum of the ligand-carrier additive and the decomposed ligand.

Finally, the elution chromatograms using the ligand-carrier method are obtained for the metal chelate, AL, and the decomposed ligand, HL, respectively.

4. EXPERIMENTAL: Calculation with a Computer

The Fortran program is used for the calculation with a FACOM 230–75 computer. The program is shown in appendix III and the calculation time required was 10 sec..   Such input data as specification of the apparent partition coefficients ($K1$, $K2$), the apparent stability constant ($K3$) and the relative amount of the carrier-gas additive (CLG) are required.   In the program, the number of plates (N) was fixed at 50 and the amount of injected sample was fixed at 1 unless specified for each discussion.   The computer output consists of the amount of chelate ($AL_{g,N}$), the amount of the ligand vapour ($HL_{g,N}$), the total of $AL_{g,N}(\sum_{t=1}^{T} AL_{g,N})$, $HL_{g,N}$ ($\sum_{t=1}^{T} HL_{g,N}$) and the total sum ($\sum_{t=1}^{T} AL_{g,N} + \sum_{t=1}^{T} HL_{g,N}$). The calculation is continued until the total sum reaches 0.999.   The number of the datum shows the number of the transfer stage (t).

In the present paper, the apparent partition coefficients, $K1$ and $K2$, are chosen to be 30 and 1, respectively; the values are presumed from the experimental results of the gas chromatography.[3,4]

5. Results and Discussion

From the calculation of the simulation on the reaction chromatography, a number of chromatogram were obtained for the various input data by the digital computer.

The input data of $CLG=0$ gave the chromatogram of the conventional gas chromatography. Fig. 2 shows the simulated chromatogram of the metal chelate having the apparent stability constant, $K3=2\times10^5$. The anomalous elution of the ligand based on the decomposition is observed at the front of the chelate peak. This chromatographic peak pattern corresponds to the experimental results of the gas chromatography of unstable metal chelates. For example, the experimental chromatogram previously reported is shown in Fig. 3[3].

The peak area of the eluted chelate is dependent on the apparent stability constant of the solute in the liquid phase, as shown in Fig. 4. Namely, the quantitative elution of
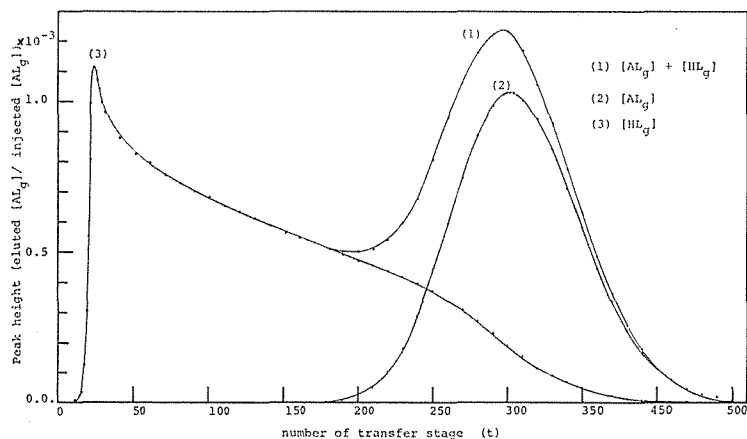

Fig. 2.   Simulated chromatogram of metal chelate (AL) on the case of the helium carrier.
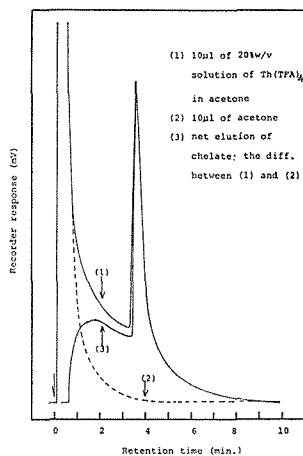$K1=30$, $K2=1$, $K3=2\times10^5$, $AL_{g,i}(i=1)$ at $t=1$: 1.0, $N=50$, $CLG=0$

Fig. 3.   Chromatogram of thorium(IV)-trifluoroacetylacetonate obtained
by using helium as carrier gas[3]

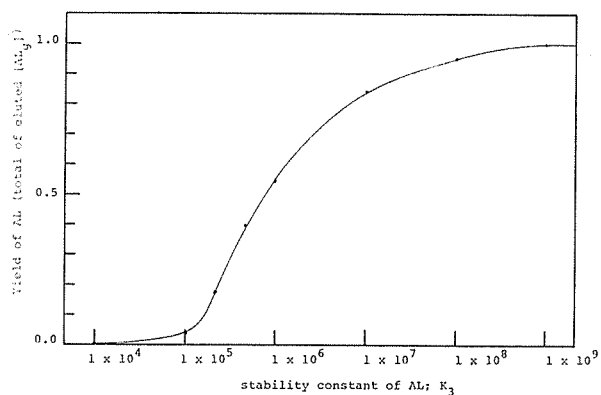Column; 2.5% Silicone XE-60/Gas Chrom-CLG (80/100) 4 mm.
i.d. ×75 cm. length

Fig. 4. Relation between the yield of AL and the stability constant of AL.
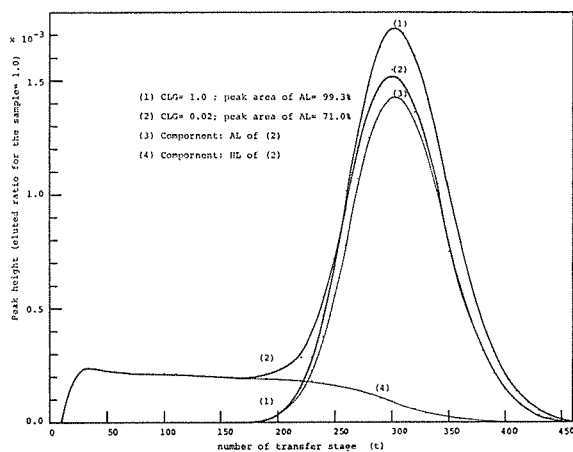$K1=30$, $K2=1$, $CLG=0.0$, $N=50$, injected $[AL_g]=1.0$

Fig. 5. Chromatograms obtained by the simulation for the ligand-carrier method.
$K1=30$, $K2=1$, $K3=2\times10^5$, $N=50$
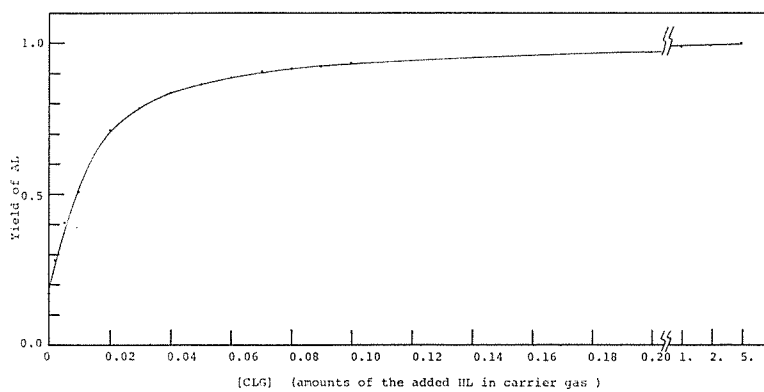

Fig. 6. Relation between the amounts of the eluted AL and the amounts
of the supplied HL
$K1=30$, $K2=1$, $K3=2\times10^5$, $N=50$

the chelate can not be expected in these chromatographic conditions (CLG=0).

When the CLG values other than zero are adopted, the anomality of the elution decreases as shown by the two simulated chromatograms in Fig. 5. The curve (1) in Fig. 5 represents the chromatogram at CLG=1, which is accompanied with little anomalous elution. The curve (2) at CLG=0.02 shows slight anomalous elution. In Fig. 5, it is also found that the number of transfer stage (retention time) of the chelate peak is scarecely influenced by the addition of the ligand vapour.

The relation between the area of the peak (yield) of the eluted chelate and the ligand vapour (CLG) is shown in Fig. 6 for the stability constant, $K3$ of 2×10^5. The corresponding experimental curve is shown in Fig. 7[4], which agrees fairly well with that of Fig. 6.

The relation between the yield of chelate and the amounts of sample is shown in Fig. 8 which is obtained from the calculation for the various amounts of the injected sample at various CLG values. From the results, it can be seen that when CLG=0 the curve does not pass through the original point and at low quantities of the sample the peak disappears,
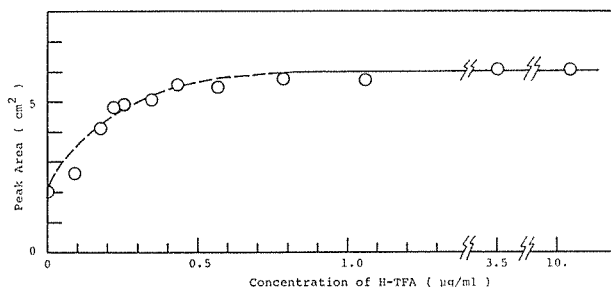

Fig. 7. Relation between the concentration of H-TFA additive in carrier
and the peak area of Co(II)-trifluoroacetylacetonate[4]

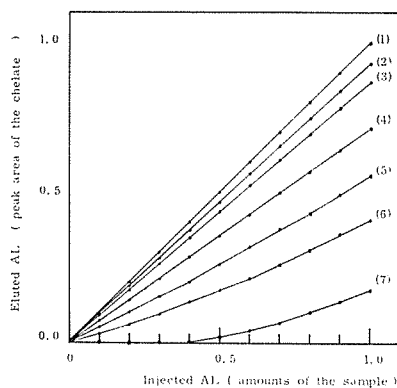Column; 5% Silicone DC-550/Celite-545

Fig. 8. Relation between the eluted AL and the injected AL
$K1$=30, $K2$=1, $K3$=2×10^5, N=50,
(1) CLG=above 1.0, (2) CLG=0.1, (3) CLG=0.05,
(4) CLG=0.02, (5) CLG=0.01, (6) CLG=0.005,
(7) CLG=0.0,

but with the increase of CLG value, the proportionality of peak area against the amount of the sample becomes improved.

6. Conclusion

In the gas chromatography of metal chelates, the chromatographic process has been simulated with a digital computer. In the computation, it was deduced that the metal chelate is dissociated in the liquid phase and releases the ligand and both the chelate and the ligand are partitioned between gas and liquid phases. The chromatograms and the yield of the eluted chelate have been calculated at various conditions. As the results, it was simulated that (1) in the case of helium carrier the anomalous chromatogram appeares, and the yield of the eluted chelate depends on the stability constant of the chelate in the liquid phase and (2) in the case of the ligand carrier, the chromatograms are improved, giving a Gaussian's curve and the relation between the yield and the quantity of the carrier-gas additive agrees well with that obtained by the experiment.

In conclusion, the simulation of the chromatographic process taking the thermal decomposition of the chelate in consideration was found extremly useful in the interpretation of the gas chromatography with carrier containing ligand vapour.

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APPENDIX I.   The symbols and the parameter

AL	metal chelate
HL	ligand vapour
A^+	chelate ion
H^+	proton of stationary liquid
g	suffix of gas phase
l	suffix of liquid phase
i	number of a cell, also used as a suffix
t	number of a transfer stage
AL_g	relative amounts of AL in gas phase
AL_l	relative amounts of AL in liquid phase
HL_g	relative amounts of HL in gas phase
HL_l	relative amounts of HL in liquid phase
A_l^+	relative amounts of A^+ in liquid phase
H_l^+	relative amounts of H^+ in liquid phase
$K1$	apparent partition coefficient of AL; AL_l/AL_g
$K2$	apparent partition coefficient of HL; HL_l/HL_g
$K3$	apparent stability constant of AL; $AL_l/(A_l^+ \cdot HL_l)$
$AK1$	$1+1/K1$
$AK2$	$1+1/K2$
$AK3$	$K3 \cdot AK1/AK2$
CLG	relative amounts of the supplied ligand vapour in gas phase
CLL	relative amounts of the supplied ligand vapour in liquid phase
$TO1$	total amounts of AL in a cell
$TO2$	total amounts of HL in a cell
N	number of the plates in a column
T	number of the transferrence of carrier gas
C_{ALG}	concentration of AL in the gas phase of a cell (mole/L)
C_{ALL}	concentration of AL in the liquid phase of a cell(mole/L)
C_{HLG}	concentration of HL in the gas phase of a cell (mole/L)
C_{HLL}	concentration of HL in the liquid phase of a cell(mole/L)
C_H^+	concentration of H^+ in the liqudi phase of a cell(mole/L)
C_A^+	concentration of A^+ in the liquid phase of a cell(mole/L)
$k1$	distribution coefficient of AL, C_{ALL}/C_{ALG}
$k2$	distribution coefficient of HL, C_{HLL}/C_{HLG}
$k3$	equilibrium constant, $C_{ALL} \cdot C_H^+/C_A^+ C_{HLL}$
V_l	volume of the liquid phase in a cell (litter)
V_g	volume of the gas phase in a cell (litter)
M	dimension parameter (mole), defined as $AL_{g,i}(i=1)/M = 1$

APPENDIX II.   The Correlation between the Model and the Real System

In the real system, $k1$ is defined by

$$k1 = C_{ALL}/C_{ALG} \tag{1}$$

in the simulation, $K1$ is defined by

$$K1 = AL_l/AL_g \tag{2}$$

the correlation between eq. (1) and (2) is

$$K1 = \frac{AL_l}{AL_g} = \frac{AL_l \cdot M}{AL_g \cdot M} = \frac{C_{ALL}}{C_{ALG}} \cdot \frac{V_l}{V_g} = k1 \cdot \frac{V_l}{V_g} \tag{3}$$

and the following corelation is also obtained.

$$K2 = k2 \cdot \frac{V_l}{V_g} \tag{4}$$

In the real system, the following equilibrium is observed.

$$C_{ALL} + C_{H^+} \xrightarrow{k3} C_{A^+} + C_{HLL} \tag{5}$$

where $k3$ is defined by

$$k3 = \frac{C_{ALL} \cdot C_{H^+}}{C_{A^+} \cdot C_{HLL}} \tag{6}$$

and the correlation between $k3$ and $K3$ is obtained as the follows.

$$
\begin{aligned}
K3 &= \frac{AL_l}{A_l^+ \cdot HL_l} = \frac{AL_l \cdot M}{A_l^+ \cdot HL_l \cdot M^2} \cdot M \\
&= \frac{C_{ALL} \cdot V_l}{C_{A^+} \cdot C_{HLL} \cdot V_l^2} \cdot M = \frac{C_{ALL}}{C_{A^+} \cdot C_{HLL}} \cdot \frac{M}{V_l} \\
&= \frac{C_{ALL} \cdot C_{H^+}}{C_{A^+} \cdot C_{HLL}} \cdot \frac{M}{C_{H^+} \cdot V_l} = k3 \cdot \frac{M}{C_{H^+} \cdot V_l}
\end{aligned}
\tag{7}
$$

APPENDIX III.   Program for the simulation of the reaction chromatography

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C          SIMULATION OF LIGAND CARRIER GC
C          ALG/ALL=1/K1, HLG/HLL=1/K2, ALL/A*HLL=K3, CLG=CONC. OF LIGAND
           COMMON ALG(50), ALL (50), HLG(50), HLL(50), A(50), AK, AK1, AK2, ALIMT,
     1     BLIMT DIMENSION FALG(10), FHLG(10), FT(10)
           ALIMT=EXP10(-30.0)
           BLIMT=EXP10(20.0)
C          ***** YOMIKOMI *****
           READ 99, N
    99     FORMAT(15)
           DO 1 IJKLM=1, N
           READ 100, AK1, AK2, AK3, CLG
   100     FORMAT (2F10.2, 2E15.3)
           LIMIT=IFIX(AK*2.0)
C          ***** MIDASI INSATSU *****
           IF(IJKLM-1) 3,3,2
     2     PRINT 110
   110     FORMAT (1H1)
     3     IF(CLG) 5,5,4
     4     PRINT 130
   130     FORMAT (1H, 10X, '***** LIGAND CARRIER GAS CHROMATOGRAPHY *****',/)
     5     PRINT 120, AK1, AK2, AK3, CLG
   120     FORMAT (1H, 5X, 'K1=', F10.2, 5X, 'K2=', F10.2, 5X, 'K3=', E12.3, 5X, 'CLG=,
     1     E12.3,/,/)
C          ***** INITIALIZATION *****
           CLL=CLG*AK2
           AK1=1.0/AK1+1.0
           AK2=1.0/AK+1.0
           AK=AK1*AK3/AK2
           SUM1=0.0
           SUM2=0.0
           SUM3=0.0
           DO 10 I=1,50
           ALG(I)=0.0
           ALL(I)=0.0
           HLG(I)=CLG
           HLL(I)=CLL
           A(I)=0.0
    10     CONTINUE
           ALG(1)=1.0
C          ***** PARTITION GAS CHRO. RUN *****
           DO 20 L=1, LIMIT
           DO 30 J=1, 10
           DO 31 JJ=1,5
           CALL HEIKO
           IF (CLG) 43, 43, 44
    43     SUM2=SUM2+HLG(50)
           GO TO 47
    44     SUM2=SUM2+HLG(50)-CLG
    47     SUM3=SUM3+ALG(50)
           IF(JJ-5) 42,41,41
    41     IF(CLG) 45, 45, 46
    45     FT(J)=ALG(50)+HLG (50)
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```
           FHLG(J)=HLG(50)
           GL TO 48
    46     FT(J)=ALG(50)+HLG(50)-CLG
           FHLG(J)=HLG(50)-CLG
    48     FALG(J)=ALG(50)
    42     DO 50 K=1,49
           I=51-K
           ALG(I)=ALG(I-1)
           HLG(I)=HLG(I-1)
    50     CONTINUE
           ALG(1)=0.0
           HLG(1)=CLG
    31     CONTINUE
    30     CONTINUE
           SUM1=SUM2+SUM3
C          ***** DATA INSATSU *****
           PRINT 200,SUM1, SUM2, SUM3
   200     FORMAT (1H0, 3F10.3)
           PRINT 300, (FT(I), I=1,10)
   300     FORMAT (1H, 10E13.4)
           PRINT 300, (FHLG(I), I=1,10)
           PRINT 300, (FALG(I), I=1,10)
           IF(CLG) 90,90,80
    80     IF (SUM3-0.999) 20,1,1
    90     IF(SUM1-0.999) 20,1,1
    20     CONTINUE
     1     CONTINUE
           STOP
           END




           SUBROUTINE HEIKO
           COMMON ALG(50), ALL(50), HLG(50), HLL(50), A(50), AK,AK1,AK2,ALIMT,
     1     BLIMT
           DO 40 I=1,50
           TO1=ALL(I)+ALG(I)
           TO2=HLL(I)+HLG(I)
           AA=A(I)
           B=AK*(AA+TO2)+1.0
           C=4.0*AK*(AA*TO2-TO1)
           DELTA=-B+SQRT(B*B-C)
           DEL=ABS(DELTA)
           IF(DEL-ALIMT) 11,9,9
     9     IF(DEL-BLIMT)12,12,11
    11     DELTA=0.0
           GO TO 13
    12     DELTA=DELTA/(2.0*AK)
    13     TOT=TO1-DELTA
           IF(TOT-ALIMT) 14,15,15
    14     ALL(I)=0.0
           ALG(I)=0.0
           GO TO 16
    15     ALL(I)=TOT/AK1
```

```
        ALG(I)=TOT-ALL(I)
   16   TOT=TO2+DELTA
        IF(TOT-ALIMT)17,18,18
   17   HLL(I)=0.0
        HLG(I)=0.0
        GO TO 19
   18   HLL(I)=TOT/AK2
        HLG(I)=TOT-HLL(I)
   19   AA=AA+DELTA
        IF(AA-ALIMT) 21,22,22
   21   AA=0.0
   22   A(I)=AA
   40   CONTINUE
        RETURN
        END
```